UNITED STATES PATENT APPLICATION

OF

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FOR

# ELECTROCHEMICAL CELL COMPRISING LAMINATION OF ELECTRODE AND PAPER SEPARATOR MEMBERS

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## BACKGROUND OF THE INVENTION

The present invention relates to electrochemical cells, such as double-layer capacitors and rechargeable batteries, comprising opposed-polarity electrode members with an interposed electrically insulating, ion-conductive separator member. Particularly, the invention relates to such cells in which the electrode members typically comprise polymeric matrix compositions of electrochemically active materials, which electrode members are laminated, preferably by means of applied heat and pressure, to the interposed separator member to form a unitary cell body. More particularly, the invention relates to such cells in which the interposed separator member comprises a sheet of paper, such as typically used in the fabrication of canister-type electrochemical double-layer (EDL) capacitor cells, composed of matted fibers of cellulose, regenerated cellulose, or the like, which are economically desirable and have the ability to absorb and retain substantial amounts of commonly employed liquid electrolyte compositions and thereby to provide high levels of ionic conductivity in the incorporating cell. In addition, the invention provides a means for fabricating such laminated cell structures while maintaining the capability of the paper separator member to retain an optimum amount of electrolyte and yield exceptionally high ionic conductivity.

A number of laminated, polymeric electrode electrochemical cell products have previously been described. For example,

rechargeable batteries of this type are discussed in U.S. Patent 5,456,000, while supercapacitor systems are detailed in U.S. Patent 6,187,061. However, although these prior systems refer to substantially the same respective electrode compositions as may be utilized in the present invention, these earlier cells were limited to the use of polymeric separator members, principally in order to enable thermally activated cohesive lamination between the similar polymeric compositions of the electrode and separator members. While such polymeric separator members were capable, with appropriate treatment, of retaining sufficient amounts of electrolyte composition to ensure effective operation, the cost of the polymeric separator materials and their fabrication was considerably higher, and, in some applications, e.g., in high-rate EDL supercapacitors, the level of electrolyte retention and resulting ionic conductivity was significantly less than normally available with existing low-cost paper separator materials typically used in non-laminated, physically compressed canister cell devices.

Numerous sheet paper products are currently available for use as separator members in electrochemical systems. Such products include single-sheet cellulose fiber materials, as well as multi-layer products comprising cellulosic and other composition sheets of various density which ostensibly yield the desirable properties, i.e., electrolyte absorption, electronic insulation, and physical strength, of the respective component sheet materials. Separator products of this type are mentioned, for example, in U.S. Patent 6,104,600.

While such separator papers perform suitably well in the intended physical compression type of electrochemical cells, the resistance of the surfaces of these papers to interfacial adhesion with desirable cell electrode compositions, particularly in preferred thermal laminating procedures,

prevents use of these papers in the fabrication of unitary laminated cell structures. Attempts to counter this weakness by means including the application of supplementary adhesive compositions at such sheet interfaces has resulted in the greater disadvantage of occluding the otherwise advantageous natural porosity of the papers and thus greatly diminishing electrolyte transport and reducing necessary ionic conductivity of an incorporating cell.

Similar attempts to utilize coated or in situ adhesive compositions as a means of laminating single-sheet paper separator members with cell electrode members to form unitary cell structures have resulted in like unacceptably high levels of cell impedance. The present invention, on the other hand, provides a means for avoiding prior deleterious obstruction of paper separator pores due to applied adhesive compositions while enabling the formation of strong, permanent bonding between electrochemical cell electrode members and interposed paper separator members.



## SUMMARY OF THE INVENTION

Electrochemical cell members employed in the present invention are typical of previous laminated cell components, namely, a pair of laminar polymeric matrix electrode members of electrochemically active components, commonly cast from fluid coating compositions, and an interposed ion-transmissive, electron-insulative separator member. As are normally associated with the electrode members, electrically conductive current collector members, often of reticulated metallic material, are laminated to or embedded in the electrode members at a convenient stage in the fabrication procedure.

In a preferred embodiment of the present invention, opposed electrode members of an electrochemical cell are prepared with respective active material components, e.g., activated carbon in supercapacitor fabrications or ion intercalation compounds in rechargeable battery structures, dispersed in a polymeric matrix composition, e.g., a poly(vinylidene fluoride) homopolymer or its copolymer with hexafluoropropylene, chlorotrifluoroethylene, or tetrafluoroethylene incorporated with a compatible primary plasticizer.

The proportion of such plasticizer is selected to be sufficient to impart to the electrode matrix polymeric component the capability of thermoadhesive flow at preferred applied temperatures, usually in the range of about 100°C-140°C. In such a heat-activated state, the electrode polymer composition is capable of forming under pressure, e.g., with opposed platens or typical lamination rollers at about 20-40 N/cm, a physical bond with the surface of a separator member paper of cellulose, regenerated cellulose, or composite cellulosic type widely available for use in canister style capacitor devices. While the electrode matrix composition, which initially comprises about 2 to 4 parts of primary plasticizer, e.g., propylene carbonate, per part of copolymer, exhibits sufficient adhesive flow under such lamination conditions to effect a firm bond to the surface of a separator member paper, there is insufficient penetration into the pores of the paper, as is often experienced with applied fluid adhesive compositions, to significantly occlude the pores and reduce the desired absorption of later-introduced electrolyte solution into the separator member.

In an alternative fabrication procedure, a lesser portion of the electrode composition plasticizer sufficient to initiate

adhesive flow of the electrode matrix polymer at least in the interfacial separator contact region under lamination conditions is deposited in the separator paper prior to cell member assembly. In this manner, there is no polymer residue to occlude the separator paper pores after removal of plasticizer, as described below. For example, a desired amount of the plasticizer, either neat or dissolved in a solvent vehicle which will be removed prior to lamination, may be applied to the separator paper by coating, dipping, spraying, or other common means.

Subsequent to the lamination of electrode members with the interposed paper separator member to form the unitary cell structure, the laminate bond is rendered resistant to weakening in the event of subsequent exposure to vagrant heating by means of removal of the matrix plasticizer component by extraction with a selective solvent, e.g., diethyl ether, methanol, ethyl acetate, or the like to which the matrix polymer component is substantially inert, or, with more volatile plasticizer compounds, by evaporation. The unitary cell structure is then activated by imbibition of typical electrolyte solution prior to hermetic sealing in a packaging member which, due to the unitary laminated structure of the operating cell, need not take the form of prior rigid canisters, but may preferably be a variously shaped envelope of flexible packaging material, typically comprising a foil and polymer film laminate.

## DESCRIPTION OF THE INVENTION

The following exemplary compositions and fabrication procedures will typify the present invention, and, unless

otherwise noted, components of the representative compositions are proportioned on a weight basis.

Example I

A supercapacitor embodiment of the present invention was prepared with 0.125 mm thick electrode member layer material cast from a homogeneous coating composition of 37.5 parts activated carbon (ASupra - Norit Co.), 2.5 parts conductive carbon black (SP - Erachem Co.), 10.0 parts poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) (Kynar PowerFLEX LBG - TotalFinaElf), and 50.0 parts propylene carbonate (PC) plasticizer in about 100 parts acetone. Upon air-drying to remove the acetone coating vehicle, a flexible sheet of polymeric matrix activated carbon electrode material was obtained from which electrode members of desired size were readily cut.

A current collector member of aluminum expanded foil grid (Microgrid - Delker Corp.) was laminated to one surface of each of two electrode members in a heated compressive roller device at about 140°C and 30 N/cm, effectively embedding the grid into the electrode surface. The remaining surfaces of the electrode members were arranged in contact with the respective surfaces of a sheet of 30 μm, 9 g/m$^2$ regenerated cellulose capacitor separator paper (TF4030 - NKK, Japan), and the assemblage was passed through the roller device at about 130°C and 20 N/cm. Upon cooling, the laminated assembly exhibited a strong adhesion between the cell members which resulted in paper fiber tear during attempted separation of the members.

The laminated unitary supercapacitor cell structure was rinsed once in diethyl ether to remove by extraction the PC

plasticizer and was dried at about 80°C under vacuum. The extracted cell laminate was then hermetically sealed under inert atmosphere in an envelope of polymeric packaging film with a typical supercapacitor electrolyte solution of 1.5 M tetraethylammonium tetrafluoroborate in acetonitrile. The resulting supercapacitor exhibited an impedance of 1.7 ohm.$cm^2$ and a capacitance of 0.48 $F.cm^{-2}$, and it performed stably over numerous cycles.

Example II

As a comparative example to display the efficacy of the present invention, a supercapacitor electrode composition was prepared as in Example I with the exception that the amount of PC plasticizer was reduced to a prior typical amount of about 20 parts. The resulting sheet material was sufficiently flexible to form electrode members and to laminate effectively with embedded aluminum grid current collector members or to prior separator members of polymeric composition. However, attempted lamination of the electrode subassemblies to the selected TF4030 separator paper member under the conditions of Example I provided only marginally acceptable physical adherence.

After solvent extraction and activation with the electrolyte solution, the resulting supercapacitor cell initially exhibited test results comparable to the earlier cell, but these results soon became erratic due to rapid loss of interfacial adhesion between electrode and separator members.

Example III

A further comparative example was prepared utilizing the electrode sheet material of Example II. In order to enhance the physical adhesion between the electrode members and the paper

separator member, the latter was pretreated by application of a polymer solution which was anticipated to provide a compatible film surface conducive to adhesion with the polymeric matrix of the electrode member composition. To this end, the TF4030 separator paper was coated with a 5% acetone solution of the same PVdF-HFP copolymer as that used for the electrode matrix.

The thermal lamination procedures employed previously provide the desired improvement in physical adhesion between the electrode and separator members; however, under performance testing the activated cell exhibited an elevated impedance of 1.9 ohm.$cm^2$ and a greatly reduced capacitance of 0.24 $F.cm^{-2}$. Subsequent testing of examples of the separator paper stock pretreated with acetone containing 0% (control), 2%, and 5% PVdF-HFP revealed a significant decrease of ionic conductivity of the respective electrolyte activated papers to levels from 5.77 mS/cm (control) to 3.79 mS/cm and 2.22 mS/cm. Thus, although the copolymer taken up by the separator stock paper enhanced the adhesion to the like polymer matrix of the electrode members, the resulting occlusion of the paper pores sufficiently reduced the movement of the critical activating electrolyte solution to thus render ionic conductivity unacceptable for useful supercapacitor fabrication.

Example IV

By way of yet further comparison with prior art practices, a cell was prepared with the electrode members of Example III and a separator member of the TF4030 paper which had been pretreated, according to the present invention, with a solution of about 20% PC plasticizer in methyl alcohol. After removal of the alcohol vehicle by evaporation in air, the PC-containing separator paper member was assembled with the electrode members in the previous manner and laminated under the conditions of

Example I. The resulting unitary cell structure, after extraction, activation, and packaging as in that example, performed under testing substantially as well as its exemplary cell over an extended test period and exhibited no tendency for disruptive delamination as was observed with the plasticizer-deficient fabrication of Example II. As was evident in this example, the supplemental plasticizer provided at the electrode interfaces by the treated separator member was sufficient, with the incorporated electrode composition plasticizer component, to enable the electrode matrix polymer to achieve thermoplastic adhesion to the separator paper at the selected lamination conditions. Also, being readily removed from the separator member paper, the temporary supplemental plasticizer poses no threat to occlude the paper pores or otherwise interfere with the advantageous absorption of cell electrolyte solution.

Example V

A rechargeable battery cell embodiment of the present invention was prepared with electrode member layers comprising polymeric matrix compositions of typical active intercalation components, e.g., $LiCoO_2$ and graphite. In accordance with common practice, the thicknesses of the electrode material layers were adjusted during preparation to obtain in the final electrode members an active positive to negative material ratio of about 2.1.

In the present example, positive electrode layer material was cast from a homogeneous coating composition of 79.0 parts commercial grade $LiCoO_2$ powder (Grade CO22 - Seimi Chemical, Japan), 3.5 parts SP conductive carbon black, 6.5 parts PVdF-HFP, and 11.0 parts PC plasticizer in about 90 parts acetone. Upon air-drying to remove the acetone coating vehicle, a flexible sheet of polymeric matrix positive electrode material

was obtained. Electrode members of desired size, about 40 $cm^2$, were readily cut from this stock sheet. Two such sheets of the material were pre-laminated to an interposed aluminum foil grid current collector in the manner of Example I to yield a positive electrode member for the cell.

Negative electrode layer material was similarly prepared from a homogeneous coating composition of 72.0 parts microbead mesophase artificial graphite (MCMB 25-28 - Osaka Gas Co., Japan), 2.5 parts SP conductive carbon black, 7.5 parts PVdF-HFP, and 18.0 parts PC plasticizer in about 90 parts acetone. Sized layers of the resulting material were laminated to an interposed copper foil grid current collector to yield a negative electrode member for the cell.

The respective positive and negative electrode members were incorporated into a unitary cell fabrication with an intervening separator member sheet of 26 μm, 12.5 $g/m^2$ calendered regenerated cellulose separator paper (CTF4826 - NKK, Japan) by lamination in the manner of Example I at about 125°C and 20 N/cm. The PC plasticizer of the laminated cell structure was removed by single extraction with diethyl ether in the described manner followed by drying at about 100°C under vacuum. The cell was then activated with 1 M electrolyte solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate and dimethylcarbonate (EC:DMC) and hermetically sealed in an envelope of typical flexible packaging material. The activated cell of about 40 $cm^2$ was then subjected to C/2 and C/5 rate charge/discharge cycle testing between 2.8 V and 4.2 V and exhibited steady capacity of about 120-125 mAh over the test period in excess of 100 cycles.

## Example VI

In a variant preparation procedure, a rechargeable battery cell fabricated by lamination in the manner of Example IV was heated under mild vacuum at about 70°C, as an alternative to extraction with selective solvent, in order to remove the processing plasticizer from the electrode matrix polymer and thereby reduce the cell's susceptibility to delamination under subsequent exposure to vagrant heat. The cell was then similarly activated with electrolyte solution and packaged for operation prior to testing which provided substantially identical results as the previous cell.

## Example VII

In another variant battery cell formulation, the positive electrode composition of Example V was revised by substitution of 10 parts dibutyl phthalate (DBP) in place of the PC plasticizer component of that earlier composition. The preparation of the cell electrode members was otherwise substantially similar. The resulting electrode members were assembled with a 50 μm, 15 g/m$^2$ kraft/manila fiber blend capacitor separator paper (FLM 50/0.3 - SPO Cascadec, Germany) and subjected to the lamination conditions of that previous example. The adhesion between the electrode and separator members was marginally acceptable. A second set of electrode members was prepared from the respective electrode sheet materials. These electrode members were assembled with a separator member of the same paper which had previously been pre-treated with a 20% methyl alcohol solution of supplemental PC plasticizer according to the present invention as in Example IV and the lamination procedure was repeated. Interfacial adhesion of the cell members was satisfactory and, after

extraction of plasticizers and activation with electrolyte, the cell performed substantially as well as of that of Example V.

The substance of the present invention may be implemented to achieve thermal laminating adhesion between commercial paper fiber electrochemical cell separator sheets and numerous combinations of polymer and copolymer matrix electrode compositions and compatible supplemental plasticizer materials. The wide range of suitable such component polymeric and plasticizer substances is apparent, for example, in the many useful, well-known compounds of this type which have been described in the art, such as U.S. Patent 5,540,741. The extent of these useful polymers and copolymer combinations of vinyl chloride, acrylonitrile, vinyl fluoride, vinyl acetate, styrene, vinylidene fluoride, and the like, and of the many applicable compatible plasticizers for these polymeric materials, e.g., the above exemplary propylene carbonate and mixtures of the same with homologous ethylene and butylene carbonate, butyl adipate, cellosolve acetate, dimethyl ethers of diethylene or triethylene glycol, and the like, render impractical the recitation here of more than the foregoing small exemplary number of such myriad combinations which are available for the advantageous practice of the invention.

Suffice it to say that selection of suitable combinations of such electrode matrix polymers and compatible plasticizers are within the routine capabilities of and subject to the preferences of the individual formulator or fabricator of desired electrochemical cell products, and that such selection need only follow the described basic parameters of the invention which prescribe the introduction into the separator-contiguous region of electrode polymer matrix composition a sufficient amount of compatible supplemental plasticizer to render the combination of these materials capable of physical adhesion to

the separator paper under desired heat and pressure conditions of lamination, as well as the preferred subsequent removal of at least a portion of the supplemental plasticizer, as by evaporation or selective extraction, in order to elevate the flow temperature of the composition and thereby ensure against delamination under vagrant heating conditions.

It is anticipated that other embodiments and variations of the present invention will become readily apparent to the skilled artisan in the light of the foregoing description and examples, and it is intended that such embodiments and variations likewise be included within the scope of the invention as set out in the appended claims.